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UNIVERSITY OF ILLINOIS BULLETIN

Vol. V. JUNE 22, 1908 No. 30

[Entered Feb. 14, 1902, at Urbana, Ill., as second-class matter under Act of Congress July 16, 1894]

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THE MODIFICATION OF ILLINOIS COAL BY LOW TEMPERATURE DISTILLATION

BY

S. W. PARR

AND

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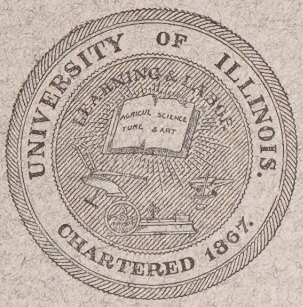

UNIVERSITY OF ILLINOIS
ENGINEERING EXPERIMENT STATION

URBANA, ILLINOIS
PUBLISHED BY THE UNIVERSITY

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UNIVERSITY OF ILLINOIS

ENGINEERING EXPERIMENT STATION

BULLETIN NO. 24 JUNE 1908

THE MODIFICATION OF ILLINOIS COAL BY LOW TEMPERATURE DISTILLATION

BY S. W. PARR, PROFESSOR OF APPLIED CHEMISTRY

AND

C. K. FRANCIS, RESEARCH FELLOW IN THE ENGINEERING EXPERIMENT STATION, DEPARTMENT OF CHEMISTRY

I. INTRODUCTION[1]

In the consumption of fuel for industrial purposes, two fundamental considerations must be kept in mind: first, there must be economy in the use of material; second, there must be regard for the comfort and health of the community. Modern practice has made marked advances in recent years in the observance of the first consideration. As might be expected, the initiative in any matter involving economy comes largely from the user, the impulse being the very natural one of self-interest. For results under the second consideration, obligatory measures, in the main, have predominated, the pressure coming from without by mandate rather than from within by preference, and advancement has been at a slower rate. Any study of conditions or of material which will promote advancement along either line is important. The present paper is a preliminary report of a series of experiments carried on in the Chemical Department of the University of Illinois, more or less continuously since 1902, having in mind primarily such a change in the chemical composition of coal as would modify or minimize the production of smoke. The facts developed thus far are mainly of scientific interest but they are such as must necessarily precede any technical study of the processes contemplated.

[1]Mainly taken from the thesis of Deane Burns, B. S., 1907, University of Illinois.

Concerning the waste of the fuel supply, there are broader reasons for economy than the mere selfish demands of the individual or corporation interested. Notwithstanding the fact that the coal fields of the United States are extensive, the coal supply is not inexhaustible. Campbell[1] states that at the present rate of increase, the available coal fields of this country will be used up in ninety years, but if the rate of consumption of 1905 remains constant the fields will last four thousand years. It is hardly possible that the great activity which has so characterized the past twenty-five years, in the building of railroads, steamship lines, and factories will be as marked in the future as it has been in the past. There will be, however, a constant increase in the consumption of coal unless some new source of power is developed. It does not seem probable that the rate of increase will be materially affected for a great many years to come; hence, Campbell estimates that four hundred years will be nearer the truth than four thousand.

The sources of loss are mainly two; one is found in wasteful methods used in the mining, and the other in the combustion of coal. Although it is not within the province of this work to discuss the present day methods of mining, it might be well to mention the fact that from 40 to 60 per cent of the coal is left in the mine in the form of walls, pillars, roofs, dust, etc. In the matter of economic combustion, the advancement has been almost entirely on the mechanical side as illustrated in the modern stokers, improved combustion chambers, the sizing and washing of coal, etc.

The idea of the modification of the chemical form of the fuel as a preparation for greater efficiency has been of slow development, but it is well illustrated in the transformation of lignites into the gaseous form for use in internal combustion engines. If it were possible to apply the same method to changing the form of coals of the bituminous type and maintain a corresponding improvement in efficiency, a great advance would be made both on the side of economy and also as related to a more sanitary and comfortable state of the atmosphere, which would result from the absence of smoke. A chemical modification of quite a different type is contemplated in this work, viz., a modification of the volatile matter either in amount or form, so that a smokeless fuel

[1]National Geo. Mag., Vol. 18, 1907.

will result and possibly also a fuel of a higher rate of efficiency in combustion.

A study of the development of coals in their various forms seems to indicate that certain natural agencies have been active, which might be made to accomplish similar results when artificially applied. The basis for some such theory may be more readily understood from a review of the various discussions of (a), coal formation, and (b), coal structure, as given below.

Formation of Coal.—Campbell[1] advances the hypothesis that the transformations of the vegetable matter into the various grades of coal are accomplished in a large measure by three factors: time, heat and crustal movements. Campbell shows that the element of time is not as important as the other two, since vegetable matter submitted to the action of molten lava, for instance, very likely undergoes rapid alteration into anthracite or natural coke, because the escaping gases are the lightest hydrocarbons, while the remaining material is the heavier or fixed carbon. Upon the other hand, if the heat is only a gradual one, or if the surrounding rocks are unbroken, the process is a slow one, as the heat is either not sufficient, or the products of distillation are not able to find a ready means of escape.

Continuing, the writer states that a study of the crustal movements does not justify the conclusion that coal was produced by distillation due to the heating effect of such movements. If, for instance, the folding of the rocks into great synclines and anticlines has changed the coal into anthracite in eastern Pennsylvania, why has not the same amount of movement in some of the isolated synclines of Pocono rocks in Maryland and Virginia produced the same result? It has not done so, and, therefore, the change to anthracite does not seem to be due alone to earth movements.

The action of heat, of course, produces fractional distillation, but whether this takes place rapidly or slowly, at a high or low temperature, the process is regulated by the surrounding or local conditions, and, since these control the process of metamorphism, they are of equal importance with the original cause. The nature of the residual product, or coal, is largely dependent upon these

[1]Economic Geology, Vol. 26, 1905.
U. S. G. S. Prof. Paper, No. 48, 1906.
Bulletin Amer. Inst. Min. Eng., March, 1906.

modifying conditions. In the first place, the extent of the change depends upon the readiness with which the gases can escape. If these are liberated as soon as they are formed, the rate of change depends upon the amount of heat applied. If, however, the vegetable matter is held between impervious layers of rock, and under great pressure, the gases can not form, and consequently, there is but little change, despite the fact that considerable heat is applied.

Campbell gives the following résumé:

1. The change from peat to lignite, from lignite to bituminous, and from bituminous to anthracite, is a process of fractional distillation due to heat.

2. The heat may be applied locally and with great intensity, as in the case of volcanic action, or it may be imperceptible, but applied throughout a long period of time.

3. In the latter case the action is so slow, and of such a nature, that it is controlled largely by conditions which accelerate or retard the process.

4. The principal conditions controlling the distillation are the porosity or the impermeability of the rocks permitting or retarding the escape of the gases formed during the process.

5. Porosity may be due either to coarseness of grain or to fissures. Where great masses are concerned, the former has little or no effect, as the rocks are practically impervious; therefore, the great controlling condition in coal metamorphism is the number of fissures. These are produced by joints and by cleavage; and where fissures are found, the coal is in a high degree of carbonization; where they are absent, it is changed only slightly from its original peaty condition.

Cross and Bevan[1], from a study of the action of sulphuric acid upon cellulose and other vegetable fibres, as well as upon coal itself, advanced the opinion that there are two possibilities as to the formation of coals. (1) The lignification of structures originally consisting of pure cellulose; (2) Such transformation may have resulted from the combination of cellulose and aromatic bodies, formed elsewhere in the plant and probably as a residue from the oxidation of hydrocarbons. Reasoning from the investigations, they have assigned to lignocellulose a formula, $C_{12}H_{18}O_9$.

[1]Phil. Mag. 352; 1882.
Jour. Amer. Chem. Soc., 55, 199; 1889.

Parr[1], from the study of cellulose and coal, reasons that during the process of decomposition, cellulose may undergo a transformation, producing lignite, ($C_{20}H_{22}O_4$); bituminous coal, ($C_{22}H_{26}O_3$); and semi-bituminous coal, ($C_{30}H_{16}O$). It may be reasonable to believe that if these various forms of coal were produced from cellulose and similar substances, and are more or less closely related, artificial methods may be devised for transforming the one into the other. While these coal molecules are, of course, hypothetical, they have their counterparts in the actual constitution of coal as shown by analyses.

Each of these theories in regard to the formation of coal offers suggestions for the production of similar results artificially. Thus, the work of Campbell shows that under conditions which permit the gases to escape, heat is of vital importance. Those of Parr show, to a certain extent, how the transition from the lower forms to the higher ones is accomplished. Given, then, the conditions favorable for the escape of the gases and heat in the correct amount, it would seem that the results of nature might be duplicated. The work of Cross and Bevan shows the influence of the original material from which the coal was produced. The character of the original vegetable matter and the different conditions under which the coal was formed, yield various results in the final products. Not all anthracite coals are alike, nor are all bituminous coals the same. Different coals, treated under identical conditions, behave in a variety of ways. These variations in the different kinds of coal can be explained only by the pure chemistry of the same.

The Constitution of Coal.—Within the last twenty-five years numerous attempts have been made to prove that coal is a definite chemical compound, or a mixture of compounds which are similar. Many chemists and investigators have succeeded in separating from coal by means of such extracting agents as ether, chloroform, benzine, pyridine, as well as by acids and alkalies, various products which show to some extent that the proximate ingredients are similar in various coals.

As early as 1805 Hatchett[2] published the results obtained from an investigation of the action of nitric acid upon coal. In

[1]Ill. Geol. Surv. Bulletin No. 3; 1906.
Jour. Amer. Chem. Soc. 28, 1425; 1906.
[2]Phil. Mag. 1805.

1879 E. Guignet[1] found that after drying coal for an hour at 110° C., and powdering it to the finest possible state, he could extract as much as four per cent with boiling phenol. The filtrate from the above was brown in color, and deposited brown flakes from the solution upon the addition of alcohol. The precipitated substance was attacked with difficulty by nitric acid, forming a yellow product. Repeated treatment of the original coal with nitric acid, filtering, evaporating the filtrate to dryness, taking the residue up with water, adding barium carbonate, filtering and removing the barium with sulphuric acid, gave a solution containing tri-nitro-resorcinol, (oxy-picric acid); oxalates were also found in the solution. Guignet believed that all coals contained a resin-like substance which, when treated with nitric acid, produced oxy-picric acid. He also found that coal contained a cellulose-like substance which was attacked by alkaline hydroxides at temperatures above 100° C.

The action of alkalies upon coals was further studied by P. F. Reinsch[2] in 1885. From a series of experiments the author comes to the conclusion that coals are composed of two substances which are characterized by their action towards alkali. That part which can be extracted by means of alkali is composed of "substances which are quite amorphous, do not exhibit signs of organic structure, possess dyeing properties, and are characterized by their resistance to the action of mineral acids". Kramer[3] considers coal to be the anhydrides of glycol and glycoic acids and their amido and oxy-derivatives.

R. T. Friswell[4] pointed out that the effect of dilute (1:2) nitric acid was to convert coal into substances which, upon drying, were "black, lustrous and very brittle, insoluble in water, but very easily soluble in ammonia and other alkali fluids. In general, these products behaved like nitro compounds". If the solutions obtained by dissolving the nitro-compound in alkali are treated with acids, a flocculent, bulky brown precipitate results, which is insoluble in mineral salts, but is soluble to some extent in pure water.

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[1] Comptes Rendus, 88, 590; 1879.
[2] Ding. Poly. Jour. 256, 224; 1885.
Jour. Chem. Soc. 876; 1885.
[3] Fisher's Jahresbericht, 113; 1887.
[4] Proc. Chem. Soc. 9, 8; 1892.

Anderson and Roberts[1] studied the action of dilute nitric acid. The product or "coal acid" was always of a definite composition, even though it might not have been composed of the same chemical individuals. Heating from 300° to 310° C. in carbon dioxide and extracting with nitric acid gives a coal acid of the same composition as the one from raw coal. In a continuation of these studies Anderson[2] concludes that "whether or not different coals contain bodies that are in a genetic or homologous series, such bodies form, at least, only a part, and it may be but a minor part of the mineral. And, furthermore, that a considerable part of the organic matter consists of a complex compound comparatively rich in nitrogen, and that above all resinous matter is always present to a small, but fairly constant degree".

P. Siepman[3] in 1891 investigated the effects of various solvents such as ether, alcohol, and chloroform upon the resinous constituents of coal. By treating a Westphalian coal of the following composition:

C = 80.31%; H = 5.50%; O and N = 12.94%; S = 1.25%, three products were obtained. That extracted by ether amounted to 0.3 per cent, after the ether extraction; 0.75 per cent more was extracted by means of chloroform; and, finally, 0.25 per cent was removed with alcohol. Two substances, which were identical, were obtained by means of ether, from two different brown coals; a fact which, in the opinion of the author, may justify the conclusion that the two products were identical and individual in body. The following table taken from the above mentioned article, shows the percentage composition of the extracted substances.

Solvents	Alcohol	Chloroform	Ether	Composition of Residue
Per cent extracted	0.25	0.75	0.30	.....
Carbon	72.52	78.82	78.74	74.00
Hydrogen	10.08	8.56	9.64	4.77
Oxygen	17.40	9.97	11.62	20.09
Sulphur	.....	.....	.....	.....
Nitrogen	.....	2.65	.....	1.14

[1]Jour. Soc. Chem. Ind., 17, 1013; 1898.
[2]Ibid, p. 1019.
[3]Ztg. f. Berg. w. Hutten, 36, 26; 1891.
Jour. Soc. Chem. Ind. 10, 753; 1891.
Ibid 10, 147; 1908.

The author further states that while the caking power of bituminous coal is considerably diminished by the above treatment, it is not entirely destroyed even though a perceptible amount of the resinous constituents of the coal is removed. Smith[1] verifies the fact that the caking power is not all destroyed by the treatment with alkali. He also studied the solvent effect of benzine. From a sample of Japanese (Miike) coal, as much as ten per cent was extracted with the above named solvent. The extracted substance was freed from benzine and subjected to fractional distillation. The portion which was distilled at 175° to 200° was naphtha. The portion distilling at 250° to 300° was treated with sodium hydroxide for phenols, then sulphuric acid was added, when a phenol of higher molecular weight was formed, having the odor of pseudocuminol. No evidences of pyridine or quinoline bases were noticed. Upon cooling the 300° fraction, paraffin scale separated out. In conclusion, the author states that the bitumen which was extracted must have come from vegetable matter different from the body of the coal. Further investigations along this line show a South American lignite, 80.1 per cent of which was soluble in benzine.[2]

Shaw[3] succeeded in nitrifying coal by submitting it to the prolonged action of a mixture of concentrated sulphuric and nitric acids. This treatment raised the "volatile matter" of the coal from 27 to 77 per cent. The "nitro coal" was quite soluble in caustic alkali and 11 per cent was soluble in methyl alcohol. Attempts to reduce the nitro coal were not successful. Luzi[4] considered that coal might be a derivative of graphitic acid.

Cross and Bevan[5] tried the oxidizing effect of hydrochloric acid and potassium perchlorate. They secured a chlorinated product which was very similar to a product obtained by treating lignitic fibres in an analogous manner. The remaining coal substance was completely soluble in caustic alkali. Smyth[6] obtained, by the use of the same reagents, products which were "acidic in properties and form a dark brown solution with caustic alkali and ammonia".

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[1]Jour. Soc. Chem. Ind., 10, 978; 1891.
[2]Ibid 17, 985; 1898.
[3]Chem. News, 74, 262; 1896.
[4]Ztg. f. Berg. w. Hutten, 38, 96; 1893.
[5]Phil. Mag. 1882.
[6]Chem. News, 74, 262; 1896.

From the preceding investigations, the following conclusions may be drawn:

1. That coal was not derived from cellulose alone, but from a combination of cellulose and aromatic bodies formed elsewhere in the plant.

2. That the main portion of coal is a definite unit, associated with a small amount of bitumen or resinous matter.

3. That the structure and properties of coal are greatly modified by the removal of certain portions of the coal by means of solvents.

Action of heat.—It has been shown that certain solvents exert a modifying influence upon coal. The action of heat is of even greater influence than that of solvents, and its application to coal will, in general, produce two results:–

1. Removal of occluded gases.

2. Volatilization of the hydrocarbons of the coal itself. To draw an accurate line between these two would be a rather difficult matter as gases are given off continually from the slightest heat treatment to the point of carbonization of the coal.

Thomas[1] showed that coal heated in a vacuum at 100° C. gave off an appreciable quantity of gas. When coal was submitted to prolonged action of heat and vacuo, not only did the quantities of gas increase, but the quality appeared to vary as the reaction progressed. Late in the action, volatile products came over which condensed to crystalline solids, showing that these hydrocarbons did not exist as such in the coal, but were products of the reactions.

Smith[2] notes that the preheating of coals destroys their caking properties.

Siepman[3] has shown that the caking properties of coal are modified by extraction of the coal with ether and chloroform. The property of "caking" is then due to the easily volatile hydrocarbons. Investigations similar to those of Thomas[4] were carried on by Bedson.[5] Eight hundred seventy grams of coal dust were treated in vacuo with the following results. The first treatment was for twenty days at a temperature of 30° C. The results, when tabulated, are as follows:

[1] Jour. Soc. Chem. Ind. 144: 1876.
[2] Ibid 10, 975; 1891.
[3] Ibid 10, 752; 1891.
[4] Ibid 144; 1876.
[5] Chem. News, 68, 187; 1893.

Time	Temperature	Volume of Gas
1.20 days	30° C.	100.9 cc N. T. P.
2.10 days	50° C.	160.6 cc N. T. P.
3.10 days	60° C.	116.3 cc N. T. P.
4.7 days	60 to 80° C.	286.0 cc N. T. P.
5.9 hrs.	100° C.	89.5 cc N. T. P.

The above amounts were all obtained from the same sample, the process being continued at a higher temperature when all the gas had been given off at the lower one. Upon analysis, the above examples gave the results in the accompanying table:–

	1	2	3	4	5
Carbon Dioxide	5.77	8.34	12.12	27.35	20.80
Oxygen	9.33	7.31	5.35	0.56	4.16
Carbon Monoxide	....	....	....	1.68	2.34
Olefins	....	0.39	0.77	2.14	4.74
Paraffins	3.16	4.95	9.39	31.86	29.80
Nitrogen	81.60	79.01	72.37	35.70	38.16

No hydrogen is given off and the oxygen content decreases as the temperature increases. Olefins are present in considerable amounts.

F. G. Trobridge[1] obtained similar results, and from a study of freshly hewn coal, came to the conclusion that such coal absorbs gases from the air, showing a particular preference towards oxygen, while at the same time it was giving off its own occluded gases. E. Bornstein[2] makes a study of the decomposition of coal at relatively low temperatures, that is, below 450° C. His results, briefly stated, show that the amounts of the aqueous distillates were in the same order as the "oxygen numbers" of the original coals. Small amounts of ammonia, hydrogen sulphide, and catechol were found in the distillates, and the residues left after distillation were of more uniform composition than the original coals. The gaseous distillates ranged in composition as follows:—

[1]Jour. Soc. Chem. Ind. 25, 1129; 1906.

[2]Verh. Ges. Deutsch. Ntf. w. Arzte 1904, II Teil. I Haefte 141. See also Chem. Central-Blatt 497; 1906.

1. Heavy hydrocarbons.....5 to 14 per cent
2. Methane and homologues....55 to 76 per cent
3. Hydrogen .....5 to 16 per cent

It is thus seen that the hydrogen is lower, and the hydrocarbons higher than in ordinary illuminating gas.

The work of Bornstein, which shows that the aqueous distillates are in the same order as the oxygen numbers, leads to a discussion of the nature of water or moisture in coal. It is a well known fact that moisture in coal is a varying quantity. Campbell,[1] in discussing this, says, "This is a phase of the subject upon which there is but little available information, but enough has been done to show that coal in a finely divided state and at ordinary temperatures is very susceptible to change in atmospheric conditions, not only in regard to moisture content, but also to volatile hydrocarbons". If the water retained by an air-dried sample of coal be driven off by heat and the dried sample afterwards exposed to an atmosphere of moist air, the moisture is, to a large extent, reabsorbed at a very rapid rate. Thomas[2], in reviewing the work of Dr. Hoffman of the Canadian Geological Survey, says that part of the water in coal is very obstinately held and there is no doubt that it is in chemical combination. The water is certainly given off as such, but it is not definitely known whether the hydrogen is in direct union with the oxygen or in combination with the carbon. Cross and Bevan[3] say upon this subject that some of the carbon is doubtless in combination with the hydrogen. How much of the carbon is free and how much is in combination with hydrogen will, most likely, never be known. The oxygen is, however, generally regarded as combined with the hydrogen, but it is not probable that this is the case with the deep dry coals containing occluded methane; some oxy-carbon compound containing hydrogen is probably present. The action of heat upon the coal will differ according as the hydrogen and oxygen are in direct union with each other or are in a position free to unite with each other and form water.

Parr[4] reasons that volatile matter from coal is composed of two portions; the one composed of certain compounds of carbon

[1]Econ. Geol., 1, 29; 1905.
[2]Chem. News, 70, 93.
[3]Phil. Mag. 352; 1882
[4]Ill. Geol. Surv. Bulletin No. 3; 1906.

and hydrogen which are combustible, and the other "a compound of hydrogen and oxygen in the proper ratio to form water, and hence, non-combustible". It is obvious then that if the hydrogen and oxygen are already in combination in the coal, the water thus formed simply increases the extraneous matter in the coal. Since the value of a fuel depends upon the amount of material in the same, capable of being oxidized, it is reasonable to say that this water serves no purpose. For economy's sake fuel should be as concentrated as possible, since there would be a saving in freight, as well as a more efficient combustion in the furnace. For two equal weights of the same oxidizable material, the one containing the less inert matter will tend to have the higher thermal efficiency.

Coalite.—During the year 1907 a good deal of notice was given in the British press to a product which is of interest in this connection. The following description is abstracted from a series of articles published in The Iron and Coal Trades Review, during 1907. The process for making coalite has been patented in the United States, England and Germany. The British patent claims that the method consists in subjecting any bituminous coal to a temperature approaching 800° F., (426° C.) in closed rectangular retorts, placed vertically in a gas-fired furnace for about eight hours, or until the illuminating gas ceases to be evolved. When illuminating gas ceases to come off, and the mass is substantially free from tarry components, the heat is suddenly arrested by the introduction of steam, and the product removed from the retort. Each retort has a capacity of 15 cwt.; and each charge yields about 11 cwt. of coalite. This may vary with different coals, but the yield will generally be about 70 per cent. According to the claims made for coalite, the yield and by-products will compare favorably with that obtained in the manufacture of illuminating gas.

The analysis of coalite is stated to be:

Ash	7 per cent
Volatile Matter	12 per cent
Fixed Carbon	80 per cent
Sulphur	1 per cent
B. t u.	13500

The samples which have been on exhibition in London resemble coke in appearance and combustion, burning with a bluish

flame. The English press seems to be unfavorably disposed towards coalite, probably on account of the claims made by the promoters, that it is superior to any form of steam coal, and because of the diligent efforts to float the stock of the company. This company is capitalized at $275,000 with permission to increase to $10,000,000, thus giving it many of the attributes of a mere stock-jobbing enterprise. The total profit is estimated, in the prospectus, at $2,500,000 a year from the production of 2,100,000 tons of coalite and the resulting gas, apart from other by-products.

The Scottish Smokeless Coal Company claim to make from non-coking smalls a fuel having an analysis practically the same as coalite. The Gas Light and Coke Company, of London advertise a smokeless fuel under the name of "carbo". The South Metropolitan Gas Company will probably place a similar product on the market. From these and other considerations, a serious question has been raised as to the validity of any patent intended to cover the process as outlined.

Mention is thus made of the main features involved in connection with "coalite" because of a certain resemblance in method to the experiments as carried on in this laboratory for the five or six years past. Our own work, however, has been directed primarily to the development of the fundamental facts and principles involved with a careful study of the chemical changes or reactions that may accompany the treatment under varying temperatures and in different atmospheres. The information resulting from such experiments is considered a necessary prerequisite to any industrial application of the process.

Preliminary Experiments on the Modification of the Composition of Coal

During the coal famine of 1902, mainly centering in the anthracite regions, but affecting all parts of the United States to a greater or less extent, certain experiments were begun here in the chemical laboratory of the University of Illinois, suggested, or at least stimulated by the events of that year. These experiments had in mind the possible modification of bituminous coal in such a manner as to eliminate largely the constituents which tend to produce smoke in combustion and which would consequently give to the material the essential properties of anthracite or semi-anthracite

coal. The results were first published in the Year Book of the Illinois State Geological Survey for 1906, under the title, "The Anthracizing of Bituminous Coal,"[1] and when tabulated showed a possible increase in the fixed carbon of 25 per cent and over. These experiments, however, were of a preliminary type and took no account of the composition of the evolved gases nor of the varying effects that might be produced by different kinds of atmosphere. The fact that there was a decided increase in the percentage of fixed carbon furnished sufficient ground for interest and a desire to know the ultimate possibilities in this direction.

In continuing these experiments, therefore, the preliminary work already referred to indicated in a general way the type of apparatus needed and the conditions under which further tests should be made. It was evident that for a proper study of the changes taking place some tests must be made in a non-oxidizing atmosphere while others should introduce that condition in order to demonstrate the effect on the various reactions involved.

Mr. Deane Burns[2], in his thesis investigations, had made use of a small metal cylinder of six to eight grams capacity, which was brought under temperature control by being fitted into a hot air bath. With this device some attempt was made to govern the kind of atmosphere in which the distillation should proceed. In the tests herein recorded, a larger furnace with definite circulation of atmosphere was provided as in the description below.

Experimental Work

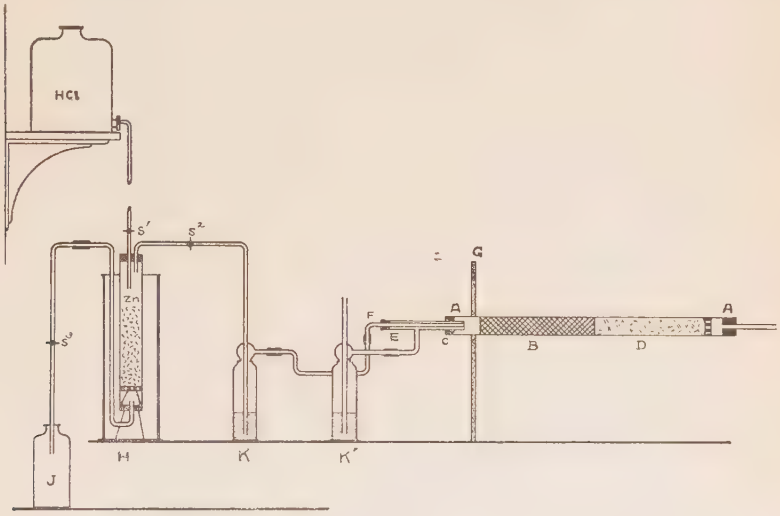
First Series: Nitrogen Atmosphere

The first series of experiments was made in a non-oxidizing atmosphere in order to eliminate, as far as possible, those variables which would result from oxidation. While this would be an extreme condition, and one not possible as an industrial feature, for experimental purposes it would admit of the study of actual changes taking place as a result of heat alone. For this purpose, therefore, nitrogen, free from carbon dioxide and oxygen, was employed. This gas was prepared from air, as suggested by Hulett[3]. The apparatus and amount of material were slightly modified, in order to permit of easy observation of the process. As claimed by the author, it is not difficult by this method to pre-

[1] Ill. State Geol. Surv. Bulletin No. 4, Year Book, 1906, p. 196.
[2] Burns, Univ. of Ill. Thesis, Class 1907.
[3] Jour. Amer. Chem. Soc. 27, 1415; 1905.

pare large quantities of nitrogen, and at a rapid rate, when once the operation is under control.

Apparatus.—The essential parts of the apparatus are shown in Fig. 1.



APPARATUS FOR PREPARING NITROGEN
FIG. 1

A. A. is an ordinary combustion tube, 2 cm. or over in diameter and 1 meter long; *B* is 40 cm. of loosely rolled copper gauze; *D* is 35 cm. of copper oxide, the wire or gauze form preferred; *E* is made from a piece of hard glass tubing; *F* is a small porcelain tube or pipe stem (a Rose crucible stem was used in our apparatus); *G* is a thick piece of asbestos board for protecting the stopper *C* from the heat: the wash bottles *K* and *K*[1] are half filled with water and serve to indicate the speed with which the air and hydrogen are being admitted. The generator *H*, devised by Messrs. McClure and Barker[1], needs but little description. The reservoir for dilute hydrochloric acid is placed about 2 meters above the table, the flow being controlled by stop cock S^1; *J* serves as a reservoir for the spent acid which siphons over from the generator.

The nitrogen was used as soon as possible after preparation and when analyzed, was found to be free from hydrogen and car-

[1]Chem. Eng. 6, 109; 1907.

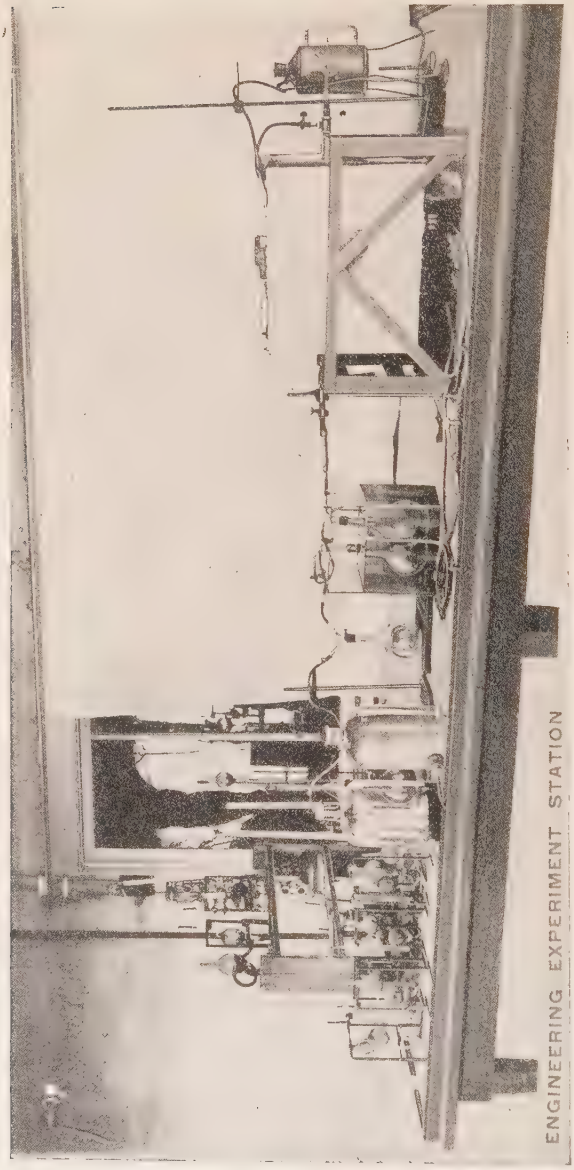
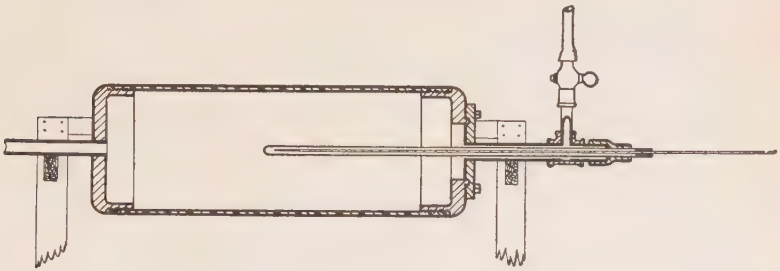


FIG. 2

bon dioxide, with but a very slight trace of oxygen, which may have been due to oxygen dissolved in the water of the gasometer.

The apparatus used for the experiments on coal is shown in Fig. 2. It consists of an iron retort placed in an oven, which is encased in asbestos. An exit tube leads into two flasks, kept cold with running water, which serve for collecting the liquid products of distillation. These flasks with their connections were weighed before each experiment; the increase in weight was called water and oil. The quantities of water and oil were determined later by separation. Beyond these is shown the safety flask, used to check any backward flow of water from the gas bottles into the condenser flasks. The details of the retort are shown in Fig. 3.



RETORT FOR LOW-TEMPERATURE COAL DISTILLATION

FIG. 3

Temperatures were indicated by a mercury thermometer, with carbon dioxide under pressure above the mercury to admit of high temperature readings. This thermometer was protected by a glass tube, which was sealed into the retort by means of a piece of thick rubber tubing, being first pulled over it, and then over the end of the retort as shown in Fig. 3. This system permitted the thermometer to be withdrawn for readings without disturbing the atmosphere in the retort.

Material.—The bituminous coal used for this series of tests was a sample of No. 7 coal from Williamson Co., Illinois (Carterville), and was marked No. 686, for identification in this laboratory. It had the following composition:–

No. 686	Moist Coal	Dry Coal
Moisture	6.53	.....
Ash	7.76	8.30
Volatile Matter	33.86	36.23
Fixed Carbon	51.85	55.47
Sulphur	2.10	2.24
B. t. u. per lb.	12380	13244
B. t. u. Ash, Water, and Sulphur Free Basis	.....	14567

The dry ash, 8.30 per cent, as shown in the above table, was used as a standard condition for reference. The results of the proximate analyses were calculated to the dry basis by subtracting the percentage of moisture from 100, dividing the remainder into each amount and multiplying by 100 to read as per cent.

$$\frac{51.85 \text{ per cent Fixed Carbon}}{(100-6.53)} \times 100 = 55.47 \text{ per cent Fixed Carbon, Dry Basis.}$$

The formula for calculating the B. t. u. in terms of "corrected" ash and water free, i. e., ash, water and sulphur free basis,[1] may be expressed as follows:

$$\frac{\text{B. t. u.} - (\text{Weight of Sulphur} \times 4050)}{100 - (\text{Ash} + H_2O + \frac{5}{8}\text{ S.})} \times 100 = \text{B. t. u. per lb. Unit Coal.}$$

Example.

$$\frac{12380 - (.0210 \times 4050)}{100 - (7.76 + 6.53 + (\frac{5}{8}\text{ S} \times 2.10)} \times 100 = 14567 \text{ B. t. u. per lb. Unit Coal.}[2]$$

Operation, Mechanical.—In preparing the sample for this series, a large quantity, about 40 pounds, of the air-dried coal was crushed to buckwheat size, thoroughly mixed and divided into several portions, each lot being numbered to correspond with the test in which it was to be used.

The operation may be described as follows: The portion of coal, usually something over 2000 grams, was placed in the retort, Fig. 3.

The head of the retort was brought to place by the screws shown, and a perfect seal secured by means of asbestos packing

[1] Jour. Amer. Chem. Soc. 28, 632; 1906.
Trans. Amer. Inst. Min. Eng. Bulletin No. 19, 49; 1908.

[2] The expression "Unit Coal" is here used to denote the ash, water and sulphur free material.

moistened with water. The apparatus, when connected, was thoroughly tested for leaks. In order to wash out the air and to furnish an inert atmosphere, nitrogen was admitted until the gas at the exit tube would no longer support combustion; usually about 15 liters were required. Heat was then applied and the evolved gases collected in the gas holders, two of these always being attached, one cut off and held in reserve to be used in case there should be an extra amount of gas suddenly evolved or when the first was filled.

The retort was turned by hand every minute or two during the operation. The exit tube was polished and coated with powdered graphite in order to permit of its turning readily within the rubber tubing which leads to the condenser flasks. When the experiment was completed the retort was disconnected from the rest of the apparatus, then sealed with rubber stoppers and slowly cooled. The gas holders and the flasks were closed by means of the pinch cocks shown in the illustration, Fig. 2.

Operation, Analytical.—The gas holders were sealed when full, the time and temperature recorded and the bottle marked. The amount of gas was easily obtained as the capacity of each bottle had been determined. Each sample was carefully analyzed according to the methods devised by Hemple.[1]

It may be advisable to mention that if the fuming sulphuric acid for the determination of illuminants shows a tendency to crystallize, slight warming, or better, dilution with water, will prevent this. Experiments seem to indicate that if this diluted acid will produce fumes and a hissing sound when added to water, it will absorb the heavy hydrocarbons. It may be of sufficient strength even when diluted with one-third its volume of water.

The coal before treatment and also the residue were analyzed according to the method recommended by the committee on coal analysis appointed by the American Chemical Society[2]. The samples of coal as freshly taken, were air-dried for twenty-four hours, carefully sampled, then powdered sufficiently to pass a 60-mesh sieve. The method for moisture was slightly modified as follows: 1 gram was weighed into a small bottle, especially designed for the purpose[3], provided with a ground glass stopper which fits over the outside edge of the bottle, thus preventing

[1]Hemple's Gas Analysis, Trans. Dennis.
[2]Jour. Amer. Chem. Soc. 21, 1130; 1899.
[3]Ill. Geol. Surv. Bulletin No. 4, 195; 1907.

loss of material by contact with the ground glass surface when the dry coal is brushed out for the ash or other determination. The bottle and contents were placed in a toluene bath, the cover removed and the sample dried for 1 hour at 105° C., the cover replaced and put in a desiccator until cold.

The following table shows the conditions under which each test was conducted:

TABLE 1

TEST CONDITIONS: CARTERVILLE COAL; NO. 686 and 791

Atmosphere of Nitrogen

Test No.	1	2	3	4	5	6	7	8
Weight of Coal in grams	2247	2278	2250	2465	2371	2400	2120	2500
Size of Coal	B.*	B.*	B.*	B.*	B.*	B.*	B.*	Nut
Period of Observation	2 hr.	2 hr. 20 m.	2 hr.	1 hr. 50 m.	4 hr.	6 hr.	3 hr.	6 hr.
Total time of Treatment	3 hr.	3 hr. 10 m.	3 hr.	2 hr. 40 m.	4 hr. 40 m.	7 hr. 30 m.	5 hr. 20 m.	8 hr.
Lowest Temperature	214°	221°	204°	243°	208°	339°	369°	364°
Highest Temperature	286°	310°	299°	358°	316°	375°	431°	400°
Average Temperature	270°	292°	277°	336°	299°	367°	402°	381°

*Buckwheat.

The figures at the top of the columns indicate the number of the test. The period of observation is the time during which the heat was maintained, as nearly as possible, at the desired temperatures. The total time of treatment includes the period of observation and the time required to bring the apparatus up to the desired temperature. The highest and lowest temperatures indicate the extremes which were recorded during the period of observation.

In the tables below, No. 2*a* and 2*b*, the actual values of the resulting product are given, in comparison with values for the original coal, in order to show the entire alterations which have occurred.

TABLE 2*a*

PROXIMATE ANALYSIS OF THE RESIDUE COMPARED WITH THAT OF THE ORIGINAL COAL. SAMPLE NO. 686

Atmosphere of Nitrogen

	Orig. Coal	1	2	3	4	5	6	7
Average Temperatures		270°	292°	277°	336°	299°	367°	402°
Moisture	6.53	1.79	1.01	1.53	1.44	1.00	0.70	1.25
Ash	7.76	8.71	8.85	8.85	8.96	8.48	9.20	10.85
Volatile Matter	33.86	33.93	33.58	34.52	30.37	34.13	25.34	19.95
Fixed Carbon	51.85	55.57	56.56	55.10	59.23	56.39	64.76	67.95
Sulphur	2.10	2.03	2.08	2.08	1.56	1.98	1.98	1.72
B. t. u.	12380	12946	13092	12980	13232	13282	13133	12836

TABLE 2*b*

PROXIMATE ANALYSIS OF THE RESIDUE COMPARED WITH THAT OF THE ORIGINAL COAL. SAMPLE NO. 791

Atmosphere of Nitrogen

	Original Coal	Test No. 8
Average Temperature		381°
Moisture	6.38	0.44
Ash	8.92	10.40
Volatile Matter	34.64	23.73
Fixed Carbon	50.06	65.43
Sulphur	2.09	1.51
B. t. u.	12443	13192

In the above tables, No. 2*a* and 2*b*, the advantages exhibited in the product, in comparison with the original coal, are exaggerated by reason of the large loss of moisture. It is, therefore, misleading as an index of actual chemical transformations, but it does give, however, a correct relative indication of values in the treated condition. For example, the resulting product, in tests 4, 5, 6 and 8, shows a relative increase in B. t. u. of from 6 to 7 per cent.

In order to arrive at an appreciation of the actual changes that have taken place, the various constituents must be calculated to some common unit for comparison. This has been done in Tables 3*a* and 3*b*, where the unit employed has been the orig-

inal ash content of the coal reduced to the dry or water free basis.

TABLE 3*a*

RESULTING CONSTITUENTS COMPARED WITH UNIT ASH, DRY BASIS
Carterville Coal. Sample No. 686
Atmosphere of Nitrogen

	Values before Heating	Test Numbers						
		1	2	3	4	5	6	7
Average Temperature		270°	292°	277°	336°	299°	367°	402°
Ash	8.30	8.30	8.30	8.30	8.30	8.30	8.30	8.30
Volatile Matter	36.23	32.33	31.49	32.38	28.13	33.38	22.86	15.26
Fixed Carbon	55.47	52.95	53.05	51.68	54.87	55.05	58.43	51.98
Sulphur	2.24	1.92	1.95	1.93	1.45	1.94	1.89	1.32
B. t. u.	13244	12366	12278	12173	12257	13000	11847	9819
B. t. u. on Unit Coal* Basis	14567	14583	14639	14601	14859	14783	14688	14702

*By Unit Coal is here meant the ash and water free basis corrected for sulphur as on p. 18.

TABLE 3*b*

RESULTING CONSTITUENTS COMPARED WITH UNIT ASH, DRY BASIS
CARTERVILLE COAL. SAMPLE NO. 791.
Atmosphere of Nitrogen

Test No. 8	Values before Heating, Dry Coal	Values after Heating, Referred to Unit Ash
Average Temperature	.....	381°
Ash	9.52	9.52
Volatile Matter	37.00	21.70
Fixed Carbon	53.47	59.88
Sulphur	2.23	1.38
B. t. u.	13290	12076
B. t. u. on Unit Coal Basis	14819	14887

In these tables it is assumed that by taking a unit ash, for example, 8.30 per cent, or the amount present in the oven-dry coal before treatment, and calculating the relative amounts of the several constituents to this unit as a basis, an indication would thus be made of the actual changes produced in the several initial values. Thus, at all temperatures, there is an actual decrease

in the volatile matter which becomes marked in the higher temperatures, viz., in tests No. 4, 6, 7 and 8, or from a range of 330° to 400° C.[1]

In tests 4 and 8, a positive increase of fixed carbon is shown, while in all cases a reduction in heat values is indicated. This reduction is accounted for by the hydrocarbon values represented in the gaseous and oil products of distillation. Especial attention should be directed to the last line, showing the heat values calculated to the unit coal basis. These values show a consistent increase throughout. A tentative explanation is offered in that the oxygen and nitrogen compounds of the volatile matter have been more largely driven off than was the case with the hydrocarbon compounds. If the loss in volatile matter, as shown, had been chiefly that of the marsh gas, (CH_4), series, a reduction in heat values for unit coal must result. If, however, the loss is made up of water of composition, there would be a relative increase in the heat content of the residual coal. The weight of water condensing in the flasks and separated from the oil, showed in each test an increase over the possible amount which could come from the free water present. The increase amounted to 3 per cent in test No. 4; 4½ per cent in test No. 6; and a little less than 3 per cent in test No. 7. These figures must represent the percentage of decrease in the water of composition. A loss of 2 per cent in this constituent would raise the B. t. u. factor, referred to the unit coal basis, from 14567 to 14864. This would seem to warrant the conclusion that a loss of water of composition occurs. This is an important point to further substantiate, as it is a fundamental feature of this investigation to develop, as nearly as may be, the conditions which govern the various decomposition processes.

In order to arrive at a further appreciation of the actual changes that have taken place, the alterations in the several constituents have been calculated to a percentage gain or loss of their original values as presented in Table 4, as below. From the table it will be seen that the actual loss in volatile matter has been accompanied in the higher temperatures, as shown in tests 6 and 8, with an actual increase of fixed carbon. The decrease in the heat units of the product is not an actual loss but is represented by corresponding values in the combustible gases as shown in a succeeding table, No. 5.

[1]Centigrade degrees are used throughout this discussion. C° x 1.8 + 32 = F°.

TABLE 4

LOSS OR GAIN OF CONSTITUENTS CALCULATED AS PERCENTAGE OF ORIGINAL VALUES FOR EACH

Atmosphere of Nitrogen. Samples No. 686 and 791

No. of Test		Volatile Matter	Fixed Carbon	Sulphur	B. t. u.	Weight, Ash and Water Free	Yield per 100 lbs. Dry Coal	Average Temperature
1	Loss	10.75	4.56	14.28	6.63	7.00	93.58	270°C
2	Loss	13.08	4.38	12.94	7.29	7.81	92.84	292°
3	Loss	10.63	6.85	13.85	8.09	8.33	92.36	277°
4	Loss	22.35	1.08	35.27	7.45	9.49	91.30	336°
5	Loss	7.86	.76	13.39	1.84	3.57	96.73	299°
6	Loss	36.90	.....	15.62	10.54	11.35	89.59	367°
	Gain	... .	5.34	.....	.....	.....	.....	...
7	Loss	57.88	6.30	41.11	25.86	26.68	75.54	402°
8	Loss	41.35	.....	38.12	9.14	9.84	91.10	381°
	Gain	.....	11.99	.....	.....	.....	.....	...

The character of the gas may be judged from the analyses given below, Table 5. No attempt was made to collect all the gas produced before Test No. 6. Although samples were taken and analyzed, they were not considered representative of the total volume, so are not given. The figures given below were obtained by averaging the analyses of each portion evolved.

TABLE 5

COMPOSITION OF GAS AS SHOWN BY AVERAGING ANALYSES OF PORTIONS GIVEN OFF

Atmosphere of Nitrogen

Test No.	6	7	8
Temperature	339°C	369°	381°
Period of Observation	6 hr.	3 hr.	6 hr.
Carbon Dioxide and Hydrogen Sulphide	21.85	17.33	12.58
Illuminants	8.67	9.54	10.48
Oxygen	0	0	0
Carbon Monoxide	8.42	7.66	6.96
Methane	2.52	32.66	28.07
Hydrogen	1.99	2.37	2.07
Nitrogen	56.54	29.97	39.50
Volume of Gas Evolved	47 L.	50 L.	45 L.

Experimental Work

SECOND SERIES: STEAM ATMOSPHERE

In this series, the atmosphere of nitrogen was replaced by one of steam. Presumably this also would be a non-oxidizing atmosphere, but the opportunity to study the action of steam directly, at the temperatures employed, as well as to compare the action with that where nitrogen was used, was deemed of sufficient importance to arrange for this series as given below.

The apparatus was set up as shown in the illustration, Fig. 2. The steam was generated from distilled water, and conducted directly into the retort, which was maintained, as before, at the desired temperature by means of gas burners, the retort being frequently turned on its axis. The coal treated was from the same mine as that used for the previous series. The composition of the samples is shown by the following analysis:

No. 1056	Moist Coal	Dry Coal
Moisture	3.28	.....
Ash	8.44	8.72
Volatile Matter	36.83	38.07
Fixed Carbon	51.45	53.19
Sulphur	2.49	2.57
B. t. u.	12868	13304
B. t. u., Unit Coal Basis		14605

The conditions under which this test was made are indicated below.

Coal No.	Test No.	Size of Coal	Weight of Coal	Period of Observation	Total Time of Treatment	Lowest Temperature	Highest Temperature	Average Temperature
1056	1	Buck-wheat	2400 g.	2 hr.	3 hr. 40 min.	366°	386°	381°

These results are very similar to those obtained in an atmosphere of nitrogen. It is to be noted that there is a relative increase in fixed carbon, (51.45 to 61.47) as also an actual increase (53.19 to 55.79). The relative heat values are higher after treat-

TABLE 6

CONSTITUENTS OF THE RESIDUE COMPARED WITH THOSE OF THE ORIGINAL COAL

Atmosphere of Steam. Temperature 381° C.

	Proximate Analyses		Unit Ash Basis	
	Before	After	Before	After
Moisture	3.28	0.28	.....	.....
Ash	8.44	9.64	8.72	8.72
Volatile Matter	36.83	28.51	38.07	25.78
Fixed Carbon	51.45	61.57	53.19	55.79
Sulphur	2.49	2.37	2.57	2.14
B. t. u.	12868	13221	13304	11959
B. t. u., "Unit Coal"			14605	14813

ment, but, when calculated to unit ash (8.72 per cent) the value is lower; the loss being represented by the hydrocarbons of the gases distilled. An interesting verification of the previous results is also shown in the B. t. u. calculated to unit coal. Here, again, it seems probable that the loss in volatile matter was greater in non-combustible constituents than in hydrocarbons. No approximation could be made in this test of the amount of water of composition recovered, because of the additional water due to the condensation of the steam. The additional weight of condensation would represent 8.30 per cent of water. In further experiments with a steam atmosphere, it may be possible to make a record of the amount of condensation from the steam introduced.

TABLE 7

ANALYSIS OF GAS EVOLVED FROM THE COAL UNDER AN ATMOSPHERE OF STEAM

Coal No.	Temperature	Period of Observation	Hydrogen Sulphide	Carbon Dioxide	Oxygen	Illuminants	Carbon Monoxide	Methane	Hydrogen	Nitrogen	Volume of Gas
1056	381°	2 hr.	20.30	12.10	0.80	7.30	9.60	20.60	0	29.30	37 L.

Experimental Work

THIRD SERIES: OXYGEN ATMOSPHERE

The operation was the same as in the previous series, except that an atmosphere of pure oxygen was supplied during the entire period of heating.

Material.—The coal treated was of the same character as No. 686, and from the same mine, with the composition shown in the following analysis.

No. 791	Moist Coal	Dry Coal
Moisture	6.13	.....
Ash	8.27	8.81
Volatile Matter	34.59	36.84
Fixed Carbon	51.01	54.21
Sulphur	2.06	2.19
B. t. u. per lb.	12443	13290
B. t. u., Unit Coal Basis	.....	14819

The following table shows the conditions under which this series was conducted.

TABLE 8

Test Conditions. Carterville Coal. Sample No. 791

Atmosphere of Oxygen

Test No.	1	2	3	4
Weight of Coal	2350 g.	2200 g.	2000 g.	2350 g.
Size of Coal	Buckwheat	Buckwheat	Buckwheat	Buckwheat
Period of Observation	3hr. 10 min.	4 hr.	4 hr. 20 min.	4 hr.
Total time of Treatment	4hr. 20 min.	5 hr. 15 min.	5 hr. 30 min.	6 hr.
Lowest Temperature	249°	328°	346°	349°
Highest Temperature	290°	358°	404°	402°
Average Temperature	279°	346°	379°	375°

The composition of the coal before and after treatment in an atmosphere of oxygen under the conditions as indicated, is shown in Table 9.

A feature to be noted in this series is the fact that, at a temperature of 279°C., only a small amount of decomposition has

TABLE 9

PROXIMATE ANALYSIS OF THE RESIDUE COMPARED WITH THE ORIGINAL COAL. SAMPLE NO. 791

Atmosphere of Oxygen

Test No.	1		2		3		4	
	Before	After	Before	After	Before	After	Before	After
Average Temperature	279°		346°		379°		375°	
Moisture	6.13	0.82	5.99	0.82	5.97	0.75	5.03	0.46
Ash	8.27	8.61	8.26	8.90	8.01	9.67	8.10	9.68
Volatile Matter	34.59	35.06	36.01	30.80	35.19	21.25	34.01	25.27
Fixed Carbon	51.01	55.51	49.74	59.48	50.83	68.33	52.86	64.59
Sulphur	2.06	2.07	1.98	1.92	2.04	1.94	2.07	2.25
B. t. u.	12565	13027	12600	13251	12600	13152	12750	13217

taken place, or, in other words, the change in the constituents is about that which would result from the removal of the moisture. At 346°, as in test No. 2, a positive decomposition has occurred. It would seem, moreover, that oxidation had played a considerable part in the changes, as may be inferred by a reference to the composition of the gases from this test, shown in Table 11. The same statements may also be made in connection with tests No. 3 and 4.

TABLE 10

RESULTING CONSTITUENTS COMPARED WITH UNIT ASH, DRY BASIS

Atmosphere of Oxygen

Test No.	1		2		3		4	
	Before	After	Before	After	Before	After	Before	After
Average Temperature	279°		346°		379°		375°	
Ash	8.81	8.81	8.78	8.78	8.52	8.52	8.52	8.52
Volatile Matter	36.84	35.87	38.30	30.38	37.42	18.72	35.81	22.20
Fixed Carbon	54.21	56.80	52.90	58.69	54.05	60.20	55.66	56.85
Sulphur	2.19	2.00	2.10	1.88	2.16	1.71	2.17	2.98
B. t. u.	13385	13330	13403	13072	13399	11588	13425	11633
B. t. u., Unit Coal Basis	14819	14497	14813	14788	14768	14793	14800	14838

In this table as in tables No. 3*a* and 3*b*, ash is used as the basis of comparison in order to show the actual variation produced in the several factors. Since the samples were not identical, a slight variation in ash makes it necessary to compare the "before" and "after" values for each test. It is interesting to note that in an atmosphere of oxygen, the same general characteristics are evident as in Series 1 and 2. This additional fact is to be noted. An examination of the gas values as given in Table 11 shows a high percentage of CO_2 for tests No. 2, 3, and 4. This indicates a direct oxidation at the temperatures employed. The amount of oxidation would doubtless be in proportion to the volume of oxygen admitted.

TABLE 11

Composition Of Gas As Shown By Averaging Analyses Of Portion Given Off

Atmosphere of Oxygen

Test No.	1	2	3	4
Average Temperature	279°	346°	379°	375°
Period of Observation	4 hr.	4 hr.	4½ hr.	3 hr.
Carbon Dioxide and Hydrogen Sulphide	5.25	20.80	12.73	13.84
Illuminants	0.00	2.50	3.53	4.24
Oxygen	13.80	10.40	9.27	7.68
Carbon Monoxide	2.50	6.60	4.74	6.64
Methane	7.20	12.27	13.68	15.16
Hydrogen	0	0	0	0
Nitrogen	71.25	47.43	56.05	52.44
Volume of Gas Evolved	12 L.	23 L.	50 L.	45 L.

The composition of the gas from one representative test in each series has been charted in Fig. 4, 5, and 6. These charts are intended to represent the analyses of different portions of the gas, the equal divisions being arbitrary. The temperatures given are those recorded when the receiver was opened for collecting the gas and when it was filled; or in other words, 109° to 184°. Fig. 4 indicates that the first portion analyzed was evolved during a range of temperature from 109° to 184°; the second portion from 184° to 375°, etc. In the case of nitrogen, (Fig. 4), and steam, (Fig. 5), the carbon dioxide shown to be present must be

looked upon as resulting from the residual oxygen in the gases or absorbed by the coal and thus being available when a sufficiently high temperature was reached.

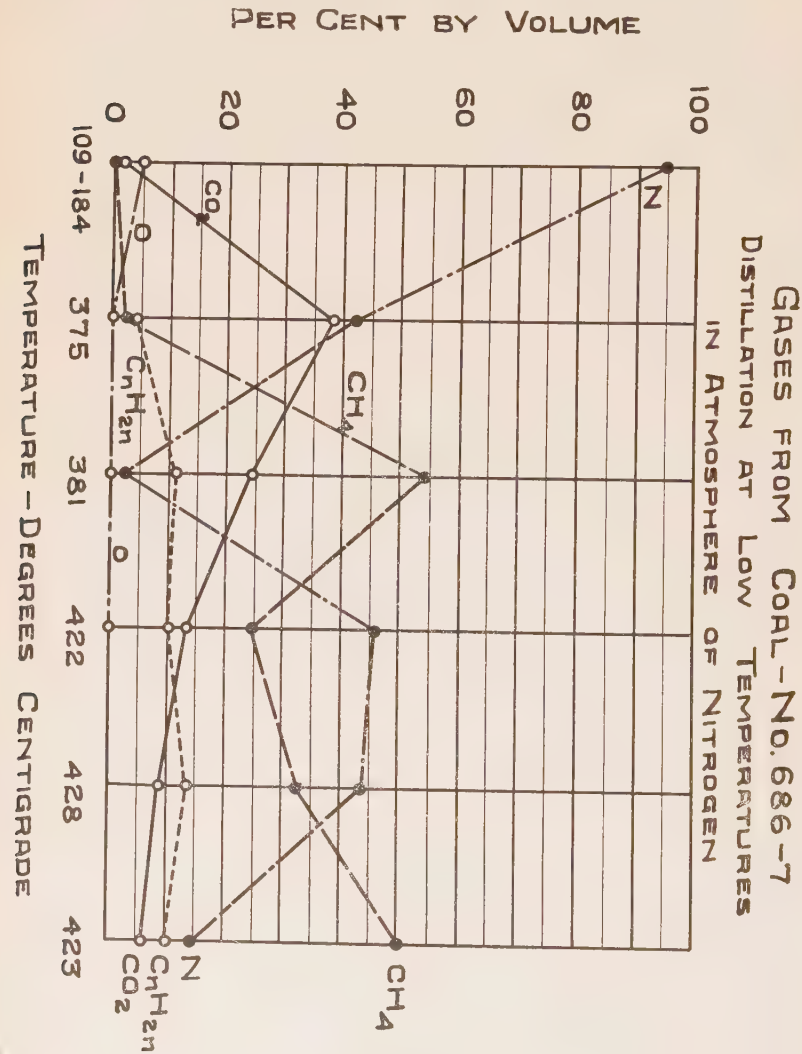


Fig. 4

Experimental Work

FOURTH SERIES: OXIDATION EXPERIMENTS

A review of all the data up to this point makes evident certain conditions which call for specific investigation. For example, Tables 5, 7 and 11, and Fig. 1, 4, 5 and 6 show the composition of the gases given off in atmospheres respectively of nitrogen, steam and oxygen. In each case a very considerable content of carbon dioxide is present, ranging in amount from 12 to 27 per cent.

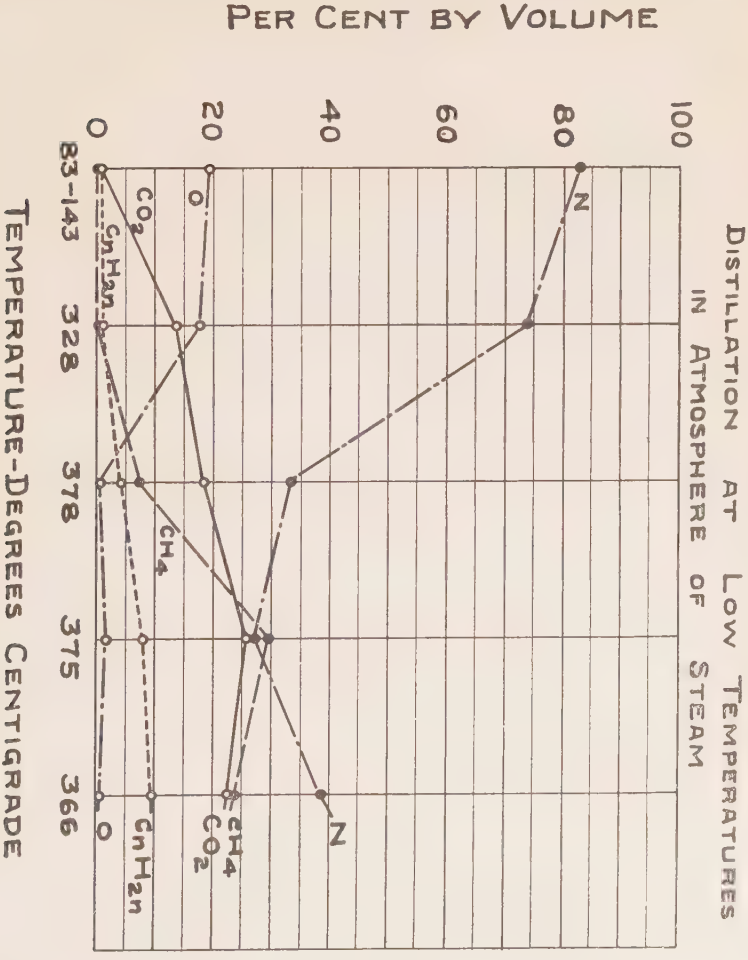


FIG. 5

Of related interest is the fact that in some of the tests with oxygen for the atmospheric medium, an occasional rise of the temperature in the retort was noted, seemingly independent of the external source of heat. This fact coupled with the marked amount of carbon dioxide in the gaseous product was positive evidence of active oxidation at the temperature of distillation. These facts

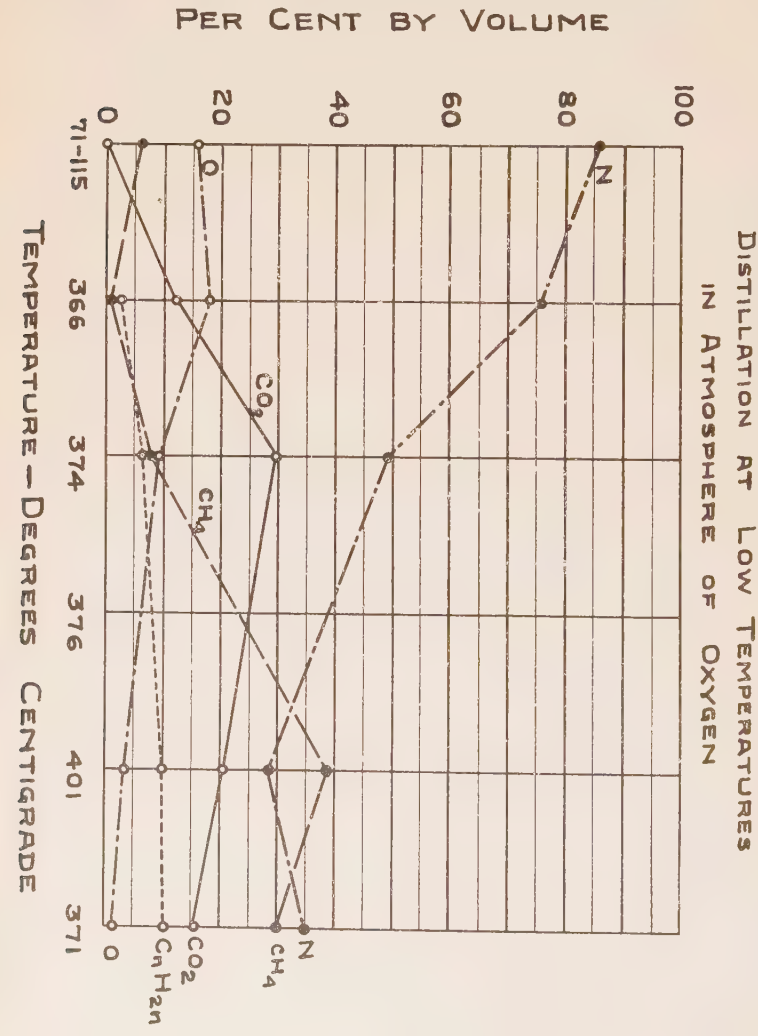
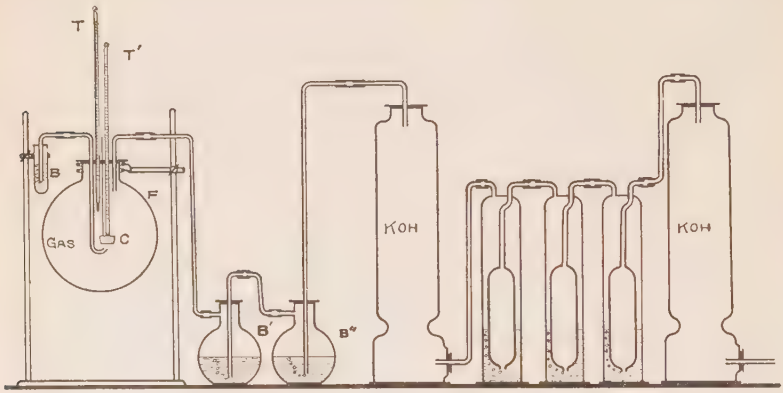


Fig. 6

also recalled certain phenomena in the earlier experiments conducted in a Rose crucible, with the thermometer bulb passing through the cover and immersed in the pulverized coal. At a certain temperature, considerably under 200°, a rise of the mercury seemed to occur, which was independent of the external source of heat. Among the tests described, where oxygen was the atmosphere used, test No. 4 showed this independent rise of temperature in a marked degree. In order to test further this evidence of oxidation, it was decided that at the end of an operation, the heat should be turned off and the retort allowed to cool slowly until a drop of, say, 50° had been recorded by the thermometer. At that point a fresh amount of oxygen was to be admitted and the temperature noted. Any rise of the thermometer would be proof of oxidation. After another drop of 50°, the test was to be repeated until a temperature was reached where no rise of the mercury would occur upon the readmission of oxygen. This would fix, broadly at least, the temperature at which active oxidation began. In following out this program, the end temperature of one test, (No. 4) was 375°. The source of heat was removed and the retort allowed to cool to 343°. Upon the readmission of oxygen copious fumes were shown at the exit tube. The thermometer was withdrawn far enough to make a reading which showed 349°. An obstruction seemingly hindered the free movement of the thermometer, necessitating its withdrawal, which was accompanied by a very marked additional rise of the mercury. The thermometer, moreover, could not be reintroduced, thus making necessary the dismantling of the apparatus. Upon opening the retort, the glass tube used to protect the thermometer was found to have been fused at a point just opposite to the oxygen inlet. By reference to Fig. 3, the relative positions of the inlet tube and thermometer may be seen. Fine particles of coal had sifted in about the protecting tube and furnished the material for the very active combustion at the point of inlet for the oxygen.

These facts suggested the desirability of a series of experiments wherein careful temperature observations could be taken with some means provided, also, for showing the presence of carbon dioxide, with a further possibility in the matter of atmospheric control which would permit the use of oxygen, steam, and air. These conditions were obtained in the following series of tests.

Apparatus.—The apparatus devised for the first tests with oxygen is shown in Fig. 7, and, as may be seen, consisted of two towers filled with solid potassium hydroxide, and three washing bottles partially filled with a 50 per cent potassium hydroxide solution. That this solution thoroughly removed any traces of carbon dioxide, which may have been contained in the oxygen, was proved by means of solutions of barium hydroxide in the two small flasks,



OXIDATION OF COAL
AND
TEMPERATURE MEASUREMENTS

FIG. 7

B' and B''. A round 1500 cc. Jena flask, F, served as a heating chamber; a nickel calorimeter capsule, C, for holding the material to be tested, was firmly fixed in a loop of heavy iron wire and suspended in the flask. Two thermometers were used, one, T, to indicate the temperature of the gas, (oxygen), and the other, T', was immersed in the coal within the capsule. The exit tube led the products into a test tube, B, containing a freshly prepared solution of barium hydroxide.

Normally, it would be expected that the temperature of the surrounding gas would be slightly higher than that of the coal, the loss by convection and poor conductivity being shown by a slightly lower reading of the thermometer imbedded in the coal. It is evident, therefore, that any relative rise in temperature, as shown by the thermometer T', would be due to chemical activity within the capsule. By charting the log of readings, therefore,

of these two thermometers, we have an index of the behavior of the coal. This plotting of the curves in the accompanying charts, therefore, shows at a glance the stages at which the changes occur, the crossing of the lines, or their relative directions, being due to the addition or removal of the exterior source of heat or to the greater or less activity of the oxidation process within the coal. This further point, however, should be borne in mind, that the temperature readings of the coal are relative as indicating the average value for the mass, since the oxidation, no doubt, is greater at the surface of the material, and the thermometer bulb must pass through zones of higher or lower temperature.

Operation.—The method of operation was as follows: Two grams of coal were placed in the nickel capsule and the thermometers, etc., adjusted as described. Oxygen was then admitted at the rate of approximately 150 bubbles per minute. The flask, *F*, was uniformly heated with a constantly moving Bunsen flame and readings of both thermometers were recorded every minute. The first appearance of carbon dioxide was noted in the test solution, *B*. This test tube was changed with sufficient frequency to indicate whether or not the evolution of carbon dioxide was continuous. It served to show also variations in quantity since it could easily be told by the rapidity of precipitation, whether the gas was increasing or diminishing in amount.

By referring now to the accompanying charts, the continuous line in each shows the reading for the surrounding gas while the dotted line gives the readings for the mass of the coal in the capsule. It may be said, also, that the readings were taken at half minute and minute intervals, but, for purposes of the charts, since the directions of the curves were not altered thereby, two minute intervals are indicated.

For convenience in charting, the results of any phenomena occurring between room temperature and those indicated, have not been employed. In most instances, however, there was a slight appearance of carbon dioxide at about 30°; this disappeared until a temperature of about 125° was reached. From this it is inferred that a certain amount of carbon dioxide was occluded in the coal and was driven off at that temperature; therefore, the first appearence of that gas was not considered to be the point where active oxidation began.

The points to be noted are as follows: The crossing of the lines frequently occurs, showing that positive oxidation of the coal is taking place. If we examine in detail, for example, Fig. 8, which is for a sample of Carterville coal in a finely pulverized form, at the point indicated by the first cross, (+) or 125°, there was a positive appearance of carbon dioxide shown by the barium hydroxide solution. This appearance of carbon dioxide continued until a temperature of 155° was reached, when the chemical activity became so great as to cause a much more positive evolution of carbon dioxide and a very rapid rise of the thermometer T'; at 168°, as indicated by the delta, △, the coal showed the presence of fire and, of course, thermometer observations could no longer be taken.

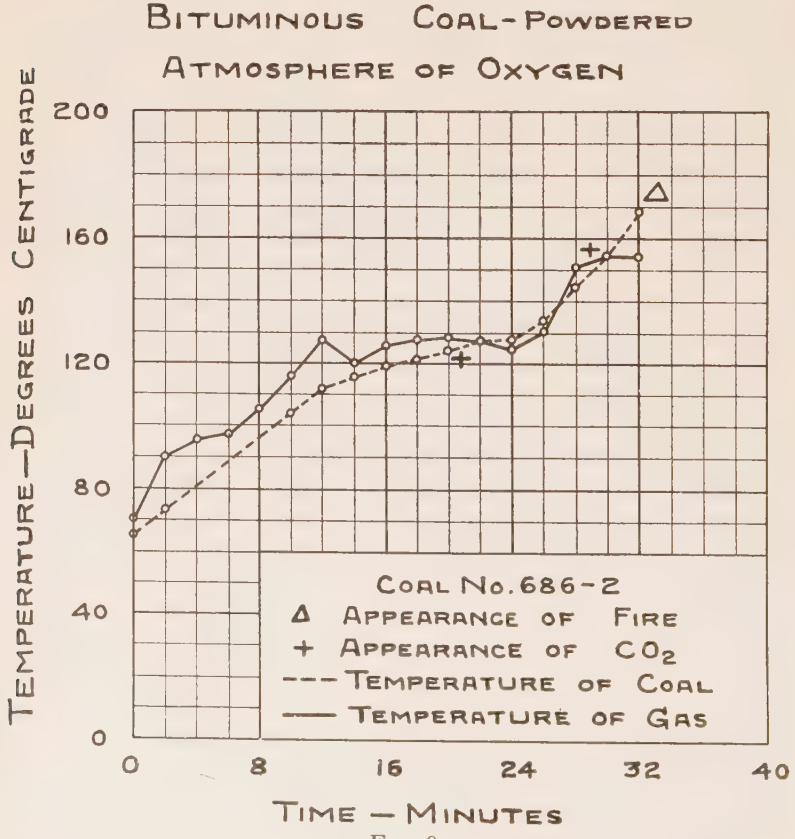


FIG. 8

Fig. 9 is a repetition of the previous tests as shown in Fig. 8, except that the coal was of buckwheat size instead of powdered. Carbon dioxide first appeared at an indicated temperature of 112° as shown by the first cross; at the second cross, which is intended to indicate the point where a very much more copious evolution of carbon dioxide appeared, the temperature reading was 147°.

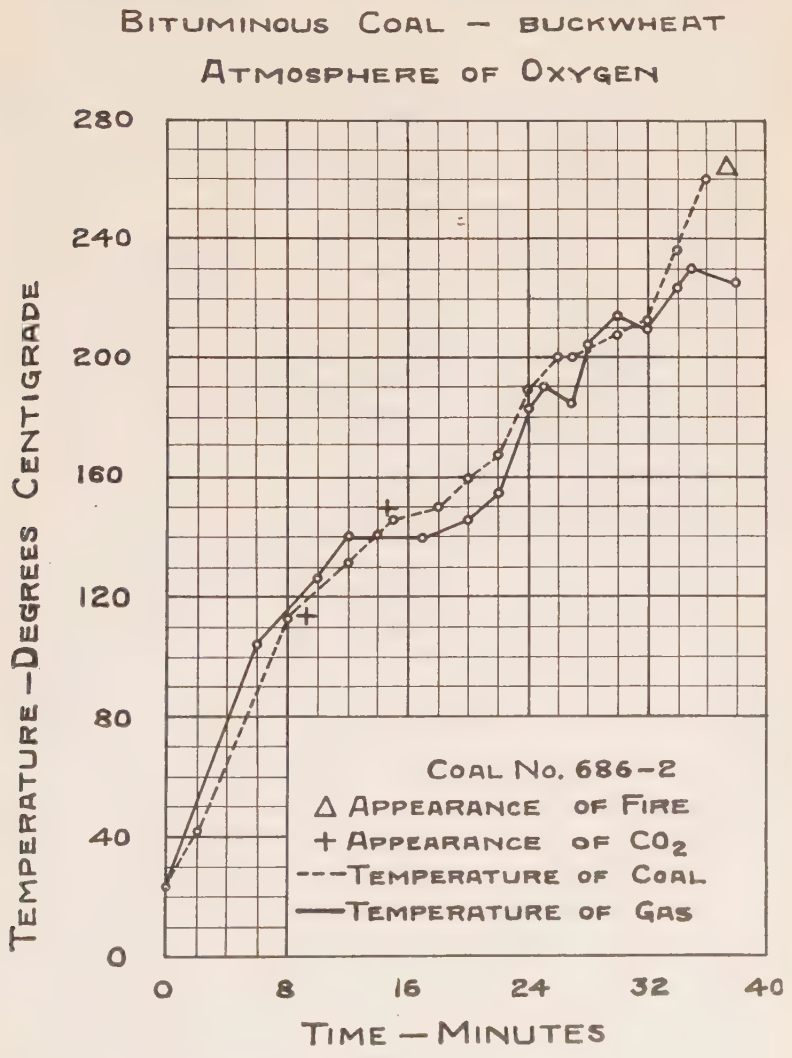


FIG. 9

This rapid evolution of carbon dioxide continued over a much longer space, however, and the activity was not sufficiently great

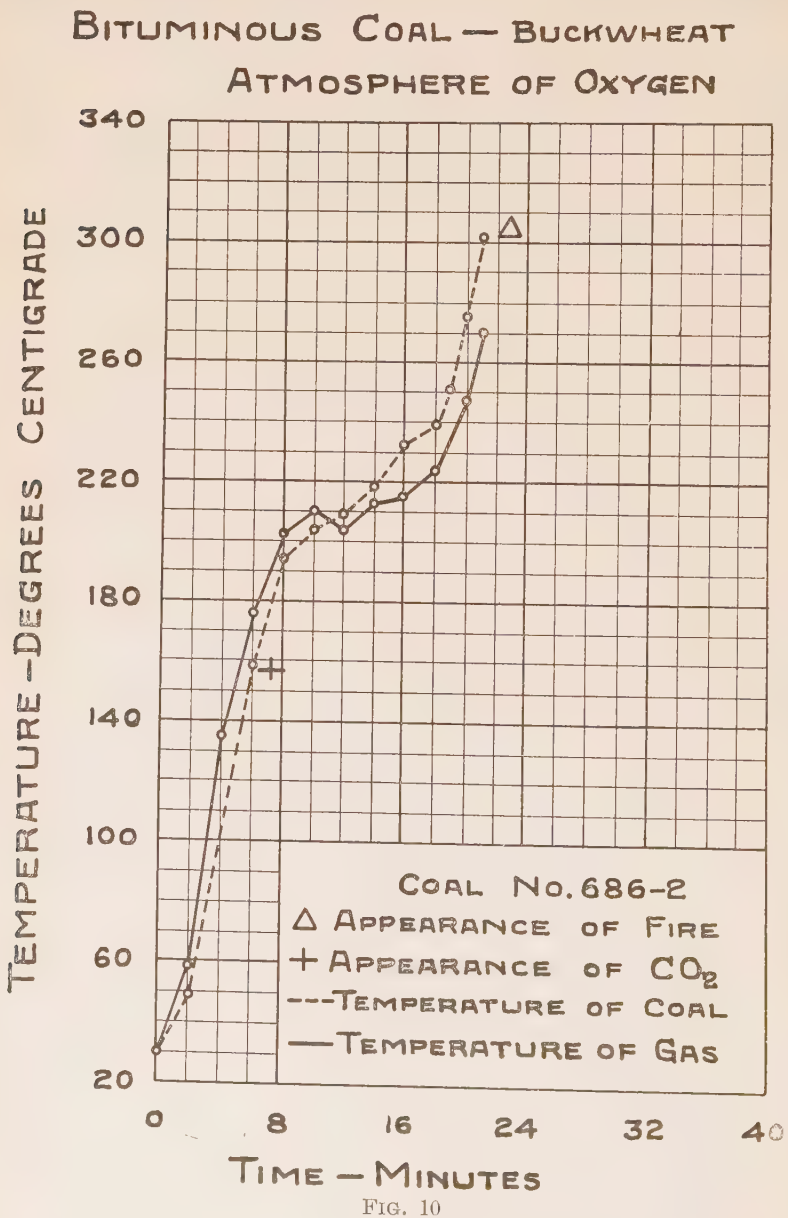


FIG. 10

to show a red glow within the coal until a temperature of 258° was reached. This simply shows that the oxidation could proceed upon the finely divided coal more rapidly than upon the buckwheat size. A duplicate test on the same coal showed a decided oxidation at 138°, but the coal did not appear to be on fire until a temperature of 300° was reached; however, the general character of the curve for this test (see Fig. 9), corresponds with the original. In the first test the temperature of the coal was higher

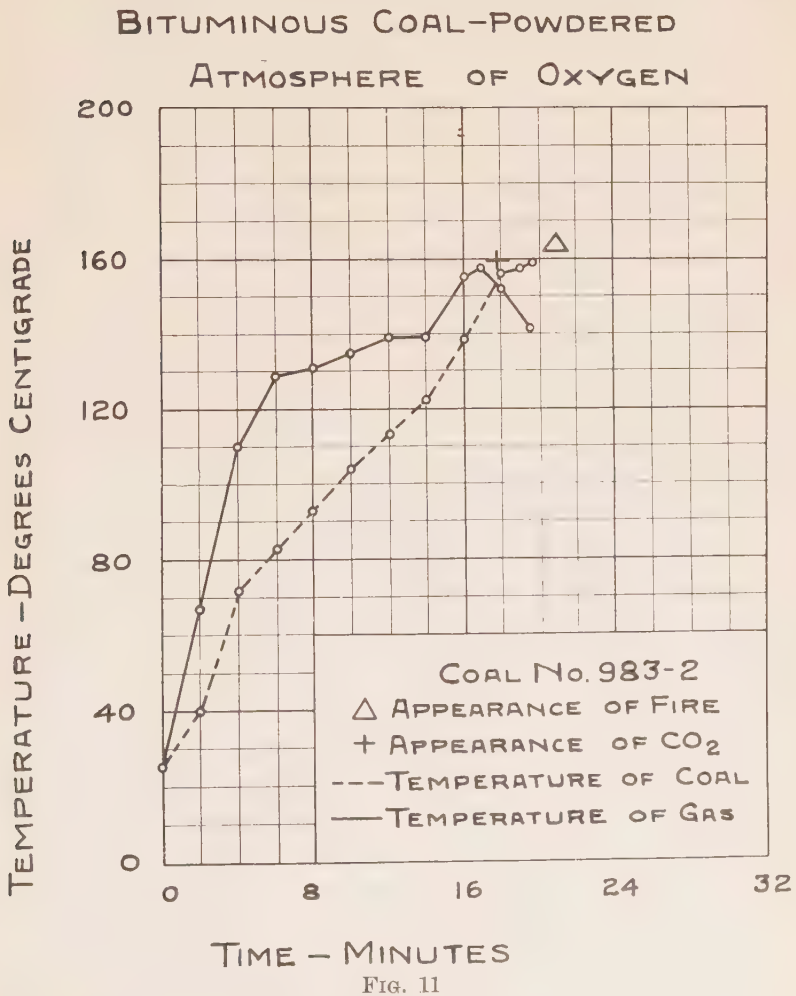


FIG. 11

than that of the gas after passing 140°, while in the second test this did not occur until 210°. This difference may have been due to the rapidity of heating, for, in the first experiment, the temperature was raised slowly, the entire time during which heat was applied being 34 minutes, while the second test was completed in 21 minutes. Under the latter conditions the oxidation was not so rapid as the increase from the external source.

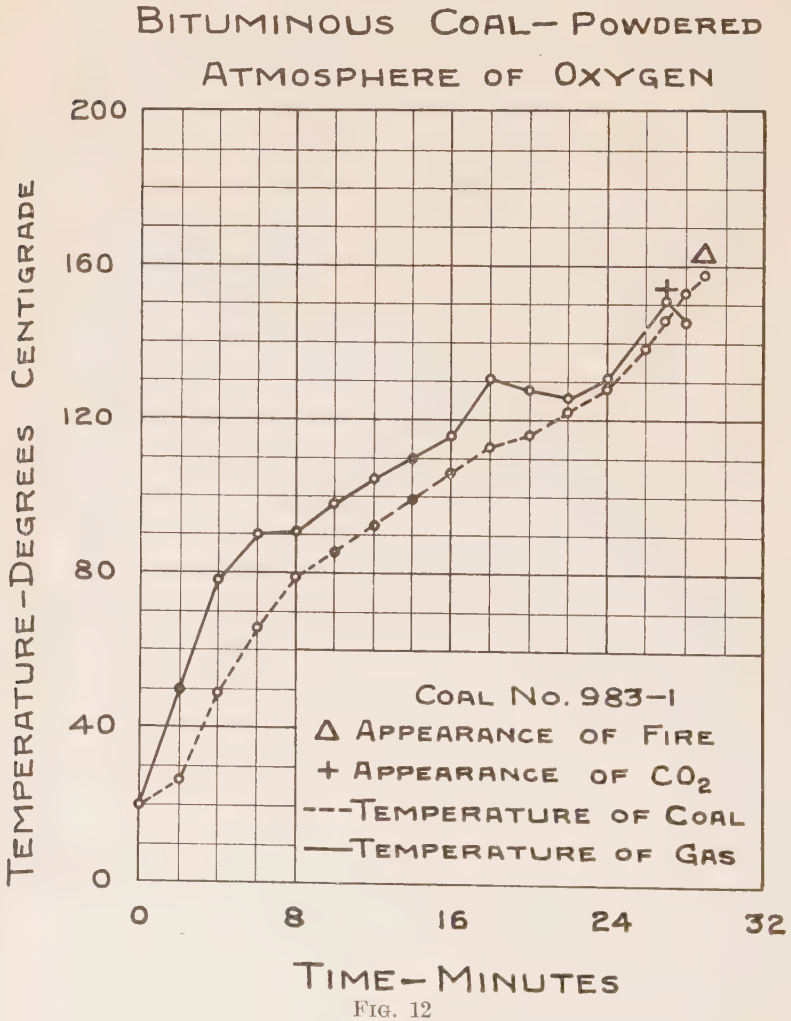


FIG. 12

Fig. 11, coal No. 983-1, represents an experiment on a sample of Taylorville, Illinois, coal in the powdered condition. The appearance of carbon dioxide was first detected at 153° C., and by reference to the chart it will be observed that at this point, the lines representing the two temperatures cross. Simultaneously, the evolution of CO_2 increased and at 157°, the coal was on fire. A second experiment on the same coal showed the point at which CO_2 was first evolved to be 156°, while the coal ignited at 158° (See Fig. 12, coal No. 983-2).

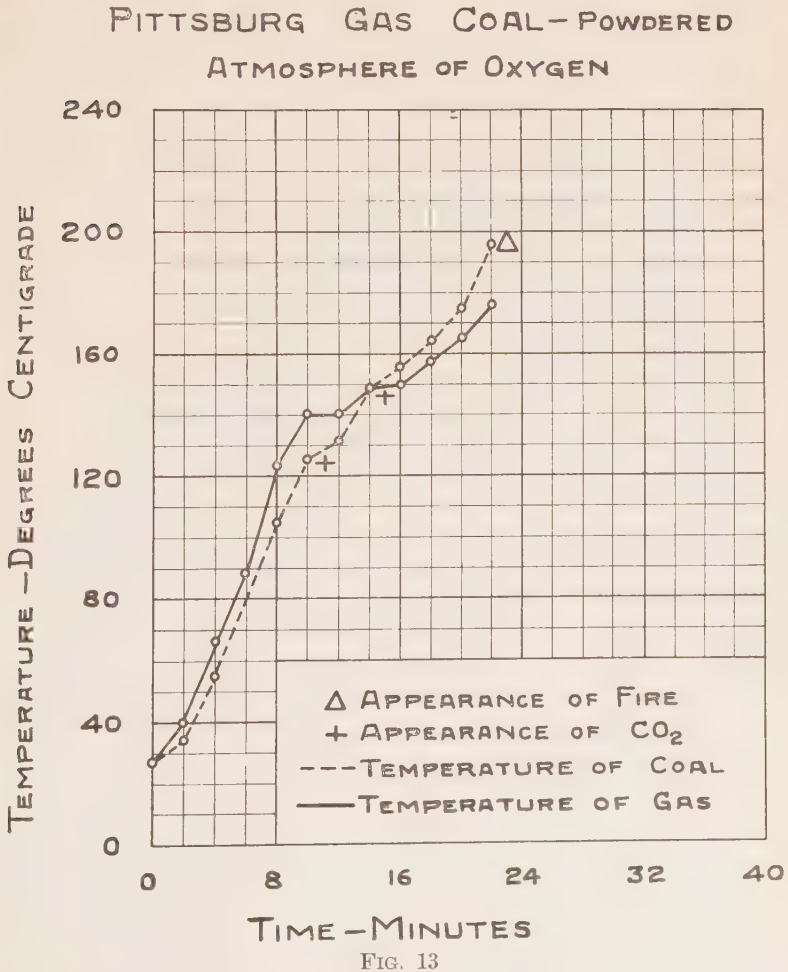


FIG. 13

Attention is called to the fact that no carbon dioxide was detected at the lower temperatures, 120° to 130°, as in the case of the other coals examined; also that the kindling temperature is practically the same as that at which the oxidation begins, as judged by the carbon dioxide produced.

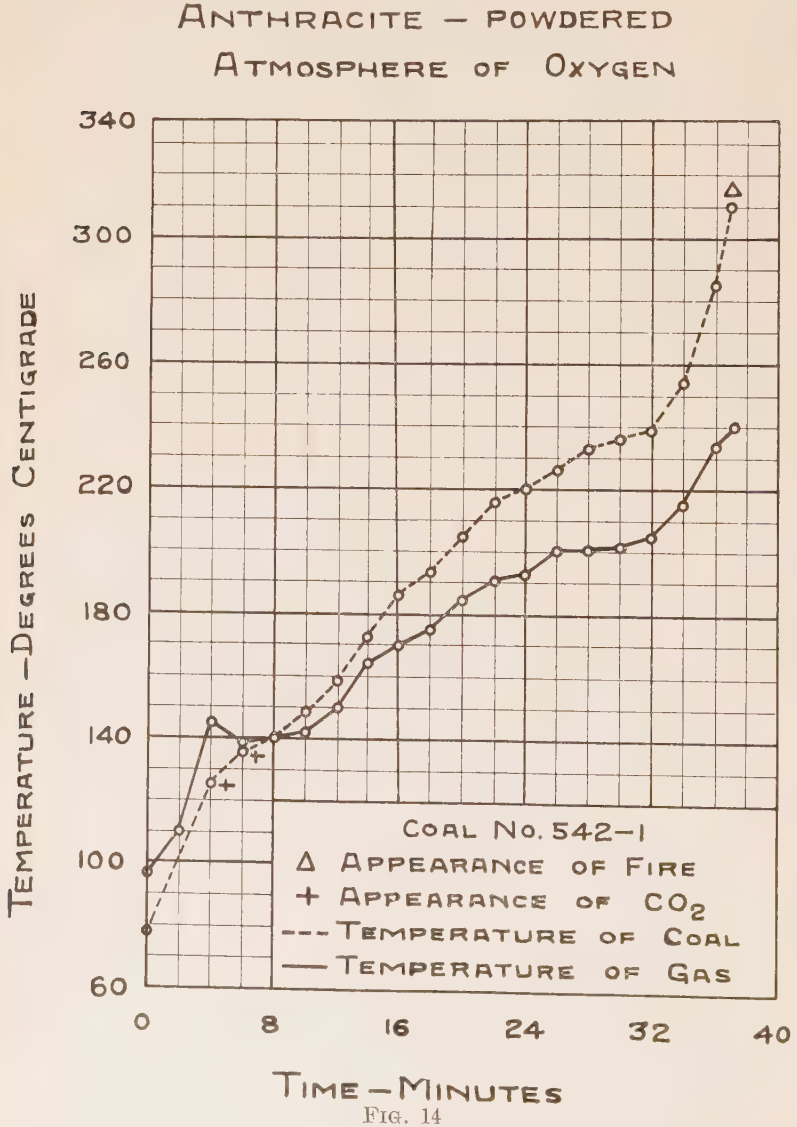


FIG. 14

In Fig. 13, a sample of Pittsburg gas coal in the powdered form, was employed. Here essentially the same phenomena were observed, as with coal 686–2 (Fig. 8), both as to the appearance of carbon dioxide and as to the more rapid evolution of the same, though the point for the appearance of fire was slightly higher than with the powdered bituminous coal of Fig. 8. This suggests that the oxidation of hydrogen may also have a part in the chemical reactions involved as being, perhaps, more readily available in coals of the strictly bituminous type.

In Fig. 14 the results are shown upon a sample of powdered anthracite. The first appearance of carbon dioxide was again at 125°. At 135° there is a stronger evolution of carbon dioxide, which continues with increasing rapidity as indicated by the more rapid rise in temperature up to 230°. At that point, a copious evolution of CO_2 occurred and ignition was indicated at 310°.

By reference to the literature of the subject, no very exact data for the kindling temperature of coal can be found. Lignite[1] is said to ignite at 150°; anthracite, when in the powdered form, at 300° or above. Another writer[2] places the ignition temperatures of cannel coal at 370° C.; lignite at 450°, and Welsh steam coal at 477°.

More recently Moissan[3], Manville[4] and others have conducted experiments upon pure amorphous carbon to determine the variations in kindling point occasioned by oscillations of temperature and as modified by varying conditions of pressure, etc. There is some resemblance between the behavior of coal as herein presented and the results by Manville upon amorphous carbon.

In order to correlate the facts of the Fourth Series with actual conditions such as would be met in the storage of coal, the atmosphere of oxygen there employed was replaced by atmospheric air. A number of tests were made using the apparatus of Fig. 7. One set of results, only, is produced, as in Fig. 15.

It will be seen that the results are not essentially different from those obtained in an atmosphere of oxygen. As would be expected, the dilution of the oxygen as in atmospheric air would retard or lessen the activity of oxidation so that the initial appearance of CO_2 was at 135° instead of at or about 120°, as in the

[1]Ding. Poly. Jour. 64, 247; 12.
[2]V. B. Lewes, J. Gas Lighting, 55, 645.
[3]Compt. Rend. 135, 921.
[4]Ibid 142, 1190.

use of oxygen. The voluminous appearance of CO_2 and the crossing of the lines occur at 165° instead of from 140° to 150°, as with oxygen. Attention is also called to the fact that at about 200° the external source of heat being withheld for a few minutes, the oxidation temperature responded to that fact and dropped back in a similar manner, showing that in order to maintain oxidation at that temperature, an external source of heat was necessary. However, at 280°, the rapid rise in the oxidation tem-

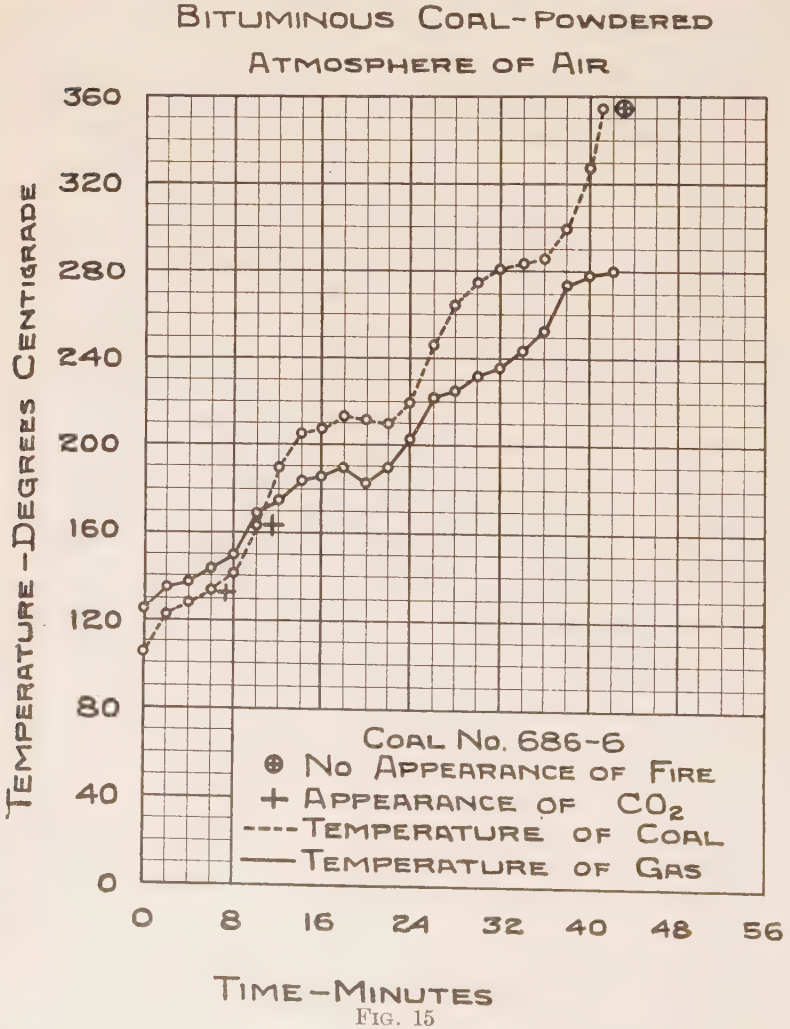


FIG. 15

perature continued, notwithstanding the cessation of the external heat. Seemingly, therefore, we have here an illustration of a type of combustion which, while still far below the ignition point, is still self-supporting and would be continuous, depending upon the oxygen supply. In another test under the same conditions essentially the same features were exhibited with the additional fact that at a temperature of 330° the coal ignited.

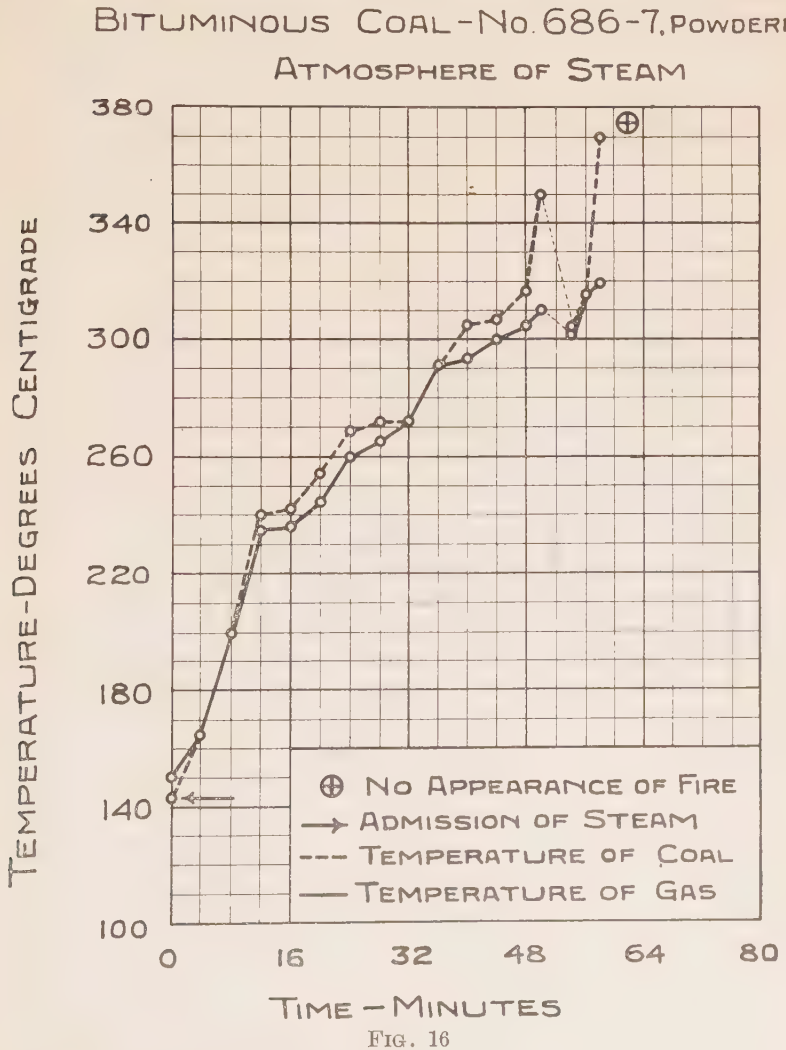


FIG. 16

Experimental Work

Fifth Series; Atmosphere of Steam

By reference again to the composition of the gases from the retort as in Table 7 and Fig. 5, it will be seen that a very considerable amount of carbon dioxide is present. This may have been due to residual oxygen in the retort and, indeed, the decrease in quantity of the carbon dioxide as the process was continued (Fig. 5), would seem to indicate some such explanation for its presence. It was deemed necessary, however, to settle positively whether in an atmosphere of pure water-vapor any such formation of carbon dioxide could occur. This feature was investigated, therefore, by use of the apparatus already described, for studying the behavior in an atmosphere of oxygen, as illustrated by Fig. 7, the substitution of steam for oxygen without the purification train being the only change. No observations were taken below 140°, and, at about that temperature, the steam was admitted into the chamber *C*, Fig. 7. Duplicate tests were made on a sample of bituminous, (Williamson County) coal in powdered form and one test on the same coal in buckwheat form. The results of only one test are charted, as in Fig. 16.

An added precaution was taken in this test to have the bulb of thermometer *T* of Fig. 7 protected by a capsule exactly as the bulb of the thermometer *T'*, and the two were placed at the same level. Also, the inlet for the steam was carried down well below both capsules and discharged near the bottom of the chamber. By this means it was sought to eliminate as far as possible any external conditions which might cause a variation in temperature as between the two thermometers. The importance of taking this extra precaution will be evident from an examination of the curve in Fig. 16. A tendency is noted at a temperature of 240° for the thermometer embedded in the coal to show a higher reading than the other. This slight advance continued with more or less uniformity, but, at about the temperature of 315°, an altogether different phenomenon was noted. At this point the mercury rose abruptly, going almost at once to the limit of the thermometer used, while the other thermometer remained constant or showed only the slight rise due to the application of external heat. After noting this sudden rise in the first instance, the heat was removed and the temperatures allowed to drop to 300°. Upon renewing

the heat, a sudden rise was again observed when 315° was reached. No appearance of carbon dioxide accompanied this rise in temperature, hence, it must be attributed to the exothermic character of the decompositions occurring at that stage. The absence of carbon dioxide throughout the test limits us, for the present, at least, to this explanation of the temperature indications in the atmosphere of steam. Similar conditions were indicated in a corresponding experiment using nitrogen, but since a small residual amount of oxygen remained in the nitrogen, giving as a result a moderate test for carbon dioxide at the exit tube, this matter of temperature differences in nitrogen must await further and more careful examination. Indeed the general proposition here indicated, of a probably exothermic behavior, is of considerable importance and calls for a carefully devised series of experiments which are now in progress.

Summary

The results thus far obtained are by no means complete but they are of sufficient interest to warrant publication in this preliminary form. Aside from the gases evolved, the by-products have received but little attention.

In the residual liquors, there seem to be no tarry compounds present but oils, phenols, ammonia, etc. Some quantitative results on the latter show as the highest result obtained from the wash liquors, about 11 per cent of the total nitrogen present in the coal. In most instances the yield was less than 1 per cent. This matter is receiving further attention.

Concerning the coal residue, enough has already been developed to indicate that it would have a special value for domestic use and such industrial operations as require a smokeless fuel. While much of the volatile constituent remains, it has undergone a change which makes it not difficult to carry on combustion without the production of smoke. This fact is, perhaps, suggested by the rather close resemblance in composition to the so-called smokeless coals. Because of the very great ease with which this material may be broken down, it would require, in all probability, to be subjected to the briquetting process.

As a rule, finely pulverized coals in contact with oxygen either diluted as in the case of air or in the pure state, begin oxidation at a temperature between 120° and 135°. In some in-

stances, however, this temperature of oxidation is higher, though in none of the tests did it exceed 155°.

The ignition temperature varies with the type of coal and to a certain extent also with the fineness of division. Finely divided bituminous coals ignite in oxygen at a temperature not far from 160°. Buckwheat sizes ignite at about 260° to 300°. Semi-bituminous coals ignite at about 200° and anthracites at about 300°.

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